

**REMARKS**

Claims 1 and 4-21 are pending in this application. Claims 11-20 are withdrawn. By this Amendment, claims 1, 4-10 and 21 are amended. The amendments to claims 1, 4-14 and 21 are supported at least by page 1, lines 9-35 and page 12, line 36 to page 13, line 4 of the original specification. Withdrawn claims 11-14 are amended for antecedence. No new matter is added by this Amendment.

**I. Interview**

The courtesies extended to Applicants' representative by Examiner Leonard and Examiner Cano at the interview held December 10, 2010, are appreciated. The reasons presented at the interview as warranting favorable action are incorporated into the remarks below, which constitute Applicants' record of the interview.

**II. Rejection Under 35 U.S.C. §112, First Paragraph**

Claims 1, 4-10 and 21 were rejected under 35 U.S.C. §112, first paragraph as allegedly failing to comply with the written description requirement. Specifically, the Patent Office alleges that the present application is directed to one-component compositions, and allegedly does not disclose any reference to a one-pack polyurethane composition.

Although Applicants respectfully disagree with the Patent Office's allegation, Applicants have amended claims 1, 4-10 and 21 to recite "a one-part polyurethane prepolymer composition." As acknowledged by the Patent Office during interview, and confirmed in the attached document (see Kirk-Othmer, ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, "Adhesives", pages 12 and 17), a one-part composition is another manner of referring to a one-component composition, which the Patent Office acknowledges is adequately described throughout the specification. See, e.g., page 1, lines 9-35 of the present specification.

Withdrawal of the rejection is requested.

**III. Rejection Under 35 U.S.C. §112, Second Paragraph**

Claims 1, 4-10 and 21 were rejected under 35 U.S.C. §112, second paragraph as allegedly being indefinite because it is allegedly unclear how the polyurethane composition produces the one-pack composition previously recited in claim 1.

Claim 1 is amended to recite "A one-part polyurethane prepolymer composition comprising, in a single part ...." As acknowledged by the Patent Office during the interview, the above amendment to claim 1 clearly indicates that the polyurethane prepolymer composition is comprised in a single part. As such, the polyurethane prepolymer composition does not produce the single part, but is contained within a single part.

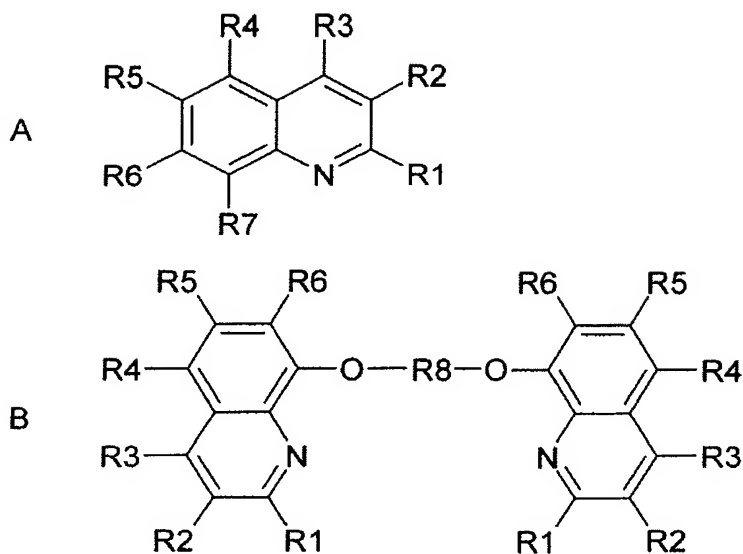
Withdrawal of the rejection is requested.

**IV. Rejections Under 35 U.S.C. §103(a)**

**A. Dammann In View Of Jayawant And In Further View Of Yoshimura**

Claims 1, 4-10 and 21 were rejected under 35 U.S.C. §103(a) as allegedly being unpatentable over U.S. Patent No. 4,788,083 ("Dammann") in view of U.S. Patent No. 3,635,906 ("Jayawant") and in further view of U.S. Patent No. 4,322,327 ("Yoshimura"). Applicants respectfully traverse the rejection.

Claim 1, as amended, recites a one-part polyurethane composition, comprising, in a single part (1) at least one polyurethane prepolymer having terminal isocyanate groups, prepared from at least one polyisocyanate with at least one polyol; and (2) at least one catalyst system obtained from components consisting of one bismuth compound and one aromatic nitrogen compound, wherein the aromatic nitrogen compound has the formula A or B,



where: R1, R2, R3, R4, R5 and R6 each independently of one another is H, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, C<sub>5</sub> to C<sub>12</sub> alkyl, COOH, COOR' or halogen, R7 is a C<sub>1</sub> to C<sub>8</sub> alkyl, a hydroxyl group (OH), O-(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>-R' with the values for x of 1-6, or O-(CH<sub>2</sub>CH(CH<sub>3</sub>)O)<sub>x</sub>-R' or a positional isomer thereof, with the values for x of 1-6, R8 is alkylene or alkylene ether, R' is alkyl, and R'' is alkyl or alkyl with heteroatoms.

In other words, claim 1 recites that the catalyst system is comprised solely of the bismuth compound and the aromatic nitrogen compound as defined in claim 1. Because Dammann, Jayawant and Yoshimura do not describe the catalyst system recited in claim 1, for the reasons discussed below, these references would not have rendered claim 1 obvious.

Dammann describes a polyurethane coating and primer composition prepared from a catalyzed reaction mixture comprised of (1) a hydroxyl containing compound, (2) an isocyanate or polyisocyanate, and (3) a complex catalyst formed from the combination of a bismuth or tin catalyst, and a complexing agent, such as a mercaptan, in the presence of tertiary amine. See Dammann, Abstract, col. 11, lines 45-65, and col. 2, lines 50-58.

As illustrated more specifically in the reaction mechanism in Figure 1 of Dammann, catalyst species II is a tin-organic catalyst having mercapto ligands. See Dammann, Figure 1

and col. 4, lines 29-40. Upon the addition of excess mercapto compounds, an equilibrium reaction is established between catalyst species II and catalyst species III, wherein the tin metal is converted from a tetracoordinate species to a hexacoordinate species. See Dammann, col. 4, lines 41-47.

Dammann further describes that the addition of an amine converts inactive catalyst species III to a more reactive catalyst species (i.e., catalyst species IV). See Dammann, col. 4, lines 53-62. In other words, the catalyst system of Dammann requires the addition of a tertiary amine activator (i.e., a chelating ligand) to convert inactive catalyst species III to active catalyst species IV, wherein the active catalyst species IV triggers the crosslinking reaction. Because the catalyst system of claim 1 is limited to the recited bismuth compound and the aromatic nitrogen compound of formula A or formula B, the catalyst system of claim 1 is different from the catalyst of Dammann. This difference was acknowledged by the Patent Office during the interview held on April 27, 2010. See May 3, 2010 Interview Summary.

Furthermore, Jayawant and Yoshimura do not remedy the deficiencies of Dammann. Jayawant further describes using a tin catalyst (i.e., not a bismuth catalyst as recited in claim 1) that has been modified with a " $\beta$ -hydroxy nitrogen-heterocyclic fused aromatic", such as 8-hydroxyquinoline, to catalyze the reaction of a polyhydroxy compound (i.e., a polyol) and a polyisocyanate. See Jayawant, Abstract, col. 4, lines 45-62 and col. 7, lines 43-73. In other words, Jayawant describes adding the functionalized tin catalyst during the reaction of the polyol and polyisocyanate.

Furthermore, Yoshimura was introduced as allegedly describing that 8-hydroxyquinoline is a known isocyanate blocking agent. See Yoshimura, Office Action, page 5 (citing Yoshimura, col. 4, lines 60-68).

However, Jayawant and Yoshimura do not describe a catalyst system obtained from components consisting of one bismuth compound and one aromatic nitrogen compound of formula A or formula B of claim 1.

For this reason, and because Jayawant describes adding 8-hydroxyquinoline to a different metal catalyst (tin instead of bismuth) and Yoshimura describes a property of 8-hydroxyquinoline, one having ordinary skill in the art would not have been provided with any reason or rationale, when reviewing Dammann, Jayawant and Yoshimura, to have combined the 8-hydroxyquinoline of Jayawant and Yoshimura with the bismuth catalyst described in Dammann, with any reasonable expectation of success.

Withdrawal of the rejection is requested.

**B. Pantone**

Claims 1, 4-10 and 21 were rejected under 35 U.S.C. §103(a) as allegedly being unpatentable over U.S. Patent No. 5,719,229 ("Pantone"). Applicants respectfully traverse this rejection.

Pantone (like Dammann, Jayawant and Yoshimura) does not describe a catalyst system obtained from components consisting of one bismuth compound and one aromatic nitrogen compound of formula A or formula B of claim 1.

Pantone describes an elastomeric polyurethane composition prepared by reacting, at an isocyanate index of 80 to 120, a) an isocyanate prepolymer prepared from polyisocyanates and polyester polyols, b) diol chain extenders, c) a catalyst and d) surface skinning agents. See Pantone, Abstract. Furthermore, Pantone (like Dammann) describes that the catalyst also includes various tertiary amine compounds having isocyanate reactive hydrogen atoms, such as triethanolamine and triisopropanolamine. See Pantone, col. 7, lines 46-54.

In other words, the catalyst system of Pantone (similar to Dammann) also requires the addition of a tertiary amine. Because the catalyst system of claim 1 is limited to the recited

bismuth compound and the aromatic nitrogen compound of formula A or formula B, the catalyst system of claim 1 is different from the catalyst of Pantone.

Pantone thus would not have provided one of ordinary skill in the art with any reason or rationale to have derived the one-part polyurethane composition recited in claim 1, with any reasonable expectation of success.

Withdrawal of the rejection is requested.

**C. Yoshimura In View Of Pantone**

Claims 1, 4-10 and 21 were rejected under 35 U.S.C. §103(a) as allegedly being unpatentable over Yoshimura in view of Pantone. Applicants respectfully traverse this rejection.

For the reasons discussed below, Yoshimura and Pantone do not describe the catalyst system recited in claim 1 and thus would not have rendered claim 1 obvious.

Yoshimura describes a urethane prepolymer composition obtained from reacting hydrophilic urethane prepolymers with a blocking agent selected from a class of heterocyclic compounds, such as 8-hydroxyquinoline. See Yoshimura, Abstract and col. 8, lines 4-24. Yoshimura further describes that additional blocking agents, such as phenol,  $\epsilon$ -caprolactam and benzophenoeoxim, may be included in the composition. In other words, the catalyst of Yoshimura allows for the presence of additional compounds in the catalyst. Because the catalyst system of claim 1 is limited to the recited bismuth compound and the aromatic nitrogen compound of formula A or formula B, the catalyst system of claim 1 is different from the catalyst system of Yoshimura.

Furthermore, as discussed above, the catalyst system of Pantone (similar to Dammann) also requires the addition of a tertiary amine. Because the catalyst system of claim 1 is limited to the recited bismuth compound and the aromatic nitrogen compound of

formula A or formula B, the catalyst system of claim 1 is also different from the catalyst of Pantone.

Withdrawal of the rejection is requested.

**V. Evidence Of Unexpected Results**

In addition to the reasons discussed above, Dammann, Jayawant, Yoshimura and Pantone do not describe the unexpected results regarding a low increase in viscosity (which translates to a good storage stability) and a fast cure (skin formation time) obtained from a one-pack polyurethane composition, such as the compositions recited in claim 1.

In the Interview Summary, the Patent Office alleged that the evidence of unexpected results (presented in Table 1 of the May 11, 2010 Amendment ("Amendment")) did not show an unexpected advantage in the viscosity increase when comparing quinoline and isoquinoline. Specifically, the Patent Office alleged that it was known from Dammann and Jayawant that isoquinoline is a known isocyanate (NCO) blocking agent and once ejected from the "pack" (or "container"), a polyurethane prepolymer composition containing isoquinoline would allegedly react slower with moisture in the air. The Patent Office concluded that this composition would have expectedly resulted in a reduced percent increase in viscosity because some of the NCO groups would have been blocked and would thus not have reacted as quickly with the moisture in the air.

Applicants respectfully disagree with the Patent Office's allegations and provide the following explanation to rebut the above allegations. Because quinoline or isoquinoline each lack amine or hydroxyl group protons, neither compound can react with an isocyanate. As such, quinoline or isoquinoline cannot be considered "blocking agents," and are instead "amine activators" that activate the reaction of isocyanates, as described in Dammann. See Dammann, col. 10, lines 50-61.

Furthermore, an increase in viscosity is based on partial curing, mainly associated with polymer chain formation. In other words, simple blocking would not increase the chain length and thus would not have an unexpected effect of the viscosity.

The details regarding the preparation of Examples 1 and 7, and Examples 9 and 10 (comparative examples), are summarized in the present specification and the Amendment. However, the testing results (i.e., the skin formation time and increase in viscosity) for Examples 1, 7, 9 and 10 are summarized below in Table 1 (and Table 1 of the original specification).

**Table 1: Skin Formation Time And Increase In Viscosity Results For Example 1, 7, 9 And 10**

	Compound L	Skin Formation Time (min)	Increase In Viscosity (%)
Example 1	tetraethylene glycol bis(8-quinolyl) ether	47	53
Example 7	8-hydroxyquinoline	84	16
Example 9 (comparative)	quinoline	85	95
Example 10 (comparative)	NONE	79	121

As seen from above, while the skin formation time remained relatively similar between Examples 7, 9 and 10, a bismuth-catalyzed polyurethane composition comprised of a catalyst system stabilized with 8-hydroxyquinoline (Example 7) instead of quinoline (Example 9) or no compound L (Example 10) resulted in an unexpected and much lower increase in viscosity. Furthermore, the skin formation time and the increase in viscosity was reduced for a bismuth-catalyzed polyurethane composition comprised of a catalyst system stabilized with tetraethylene glycol bis(8-quinolyl) ether instead of quinoline (Example 9) or no compound L (Example 10).



The above results thus demonstrate a reduced increase in the viscosity of the polyurethane composition, which effectively translates to increased storage stability. Dammann, Jayawant and Yoshimura refer to pot life (see Dammann, col. 2, lines 59-62; Jayawant, col. 1, lines 66-71; Yoshimura, col. 5, lines 59-66), which is entirely different from storage stability. Pot life is the time after mixing the materials of a two-pack polyurethane composition, such as those described in Dammann, until the composition can no longer be used as an adhesive.

Furthermore, Jayawant does not describe that the viscosity of the polyurethane decreased by the addition of 8-hydroxyquinoline (instead of using the quinoline of Dammann). Jayawant instead describes that the presence of the organo-tin catalyst (i.e., the 8-hydroxyquinoline added to tin) is used to delay the reaction between the organic polyisocyanate and an organic polyhydroxy compound (referred to in Jayawant as "time-lapse catalysis"), thereby extending the pot-life without retarding the cure rate. See Jayawant, col. 1, lines 66-71 and col. 8, lines 19-24.

For this additional reason, Dammann, Jayawant and Yoshimura do not describe the unexpected benefit of increased storage stability (i.e., reduction in the increase in viscosity).

Thus, Dammann, Jayawant, Yoshimura and Pantone do not describe the unexpected benefit of a much lower increase in viscosity for a bismuth-catalyzed polyurethane composition having a catalyst system obtained with the compounds recited in formula A or formula B of claim 1.

## **VI. Rejoinder**

In view of the foregoing amendments and arguments, Applicants respectfully request that upon allowance of claims 1, 4-10 and 21, claims 11-20 be rejoined with the present application and similarly allowed.

**VII. Conclusion**

In view of the foregoing, it is respectfully submitted that this application is in condition for allowance. Favorable reconsideration and prompt allowance of claims 1 and 4-21 are earnestly solicited.

Should the Examiner believe that anything further would be desirable in order to place this application in even better condition for allowance, the Examiner is invited to contact the undersigned at the telephone number set forth below.

Respectfully submitted,



James A. Oliff  
Registration No. 27,075

Jeremy D. Tillman  
Registration No. 62,639

JAO:JDT/hs

Attachment:

Kirk-Othmer, ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY, "Adhesives"

Date: January 3, 2011

**OLIFF & BERRIDGE, PLC**  
**P.O. Box 320850**  
**Alexandria, Virginia 22320-4850**  
**Telephone: (703) 836-6400**

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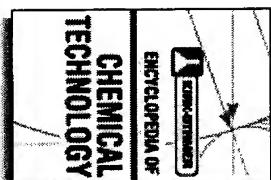
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# ADHESIVES

## 1. Introduction

An adhesive is a material used to join two or more other materials (often called adherends) through surface attachment to form a final assembly. In the simplest case, the assembly is called an adhesive joint or adhesive bond. Adhesives can be made from any material that displays the properties required for an adhesive, which include the following: adhesion (the ability to “surface attach”), the adhesive handling characteristics (so that it can be easily and economically applied to the adherends), adhesive curing characteristics (if any), and the strength of the final assembly. In this article, we describe various chemistries that have been used to obtain the wide variety of adhesives that are available.

Adhesives can be classified in many ways. Here they are classified loosely by strength. Thus, the article is divided into classes of adhesives that are based on the strength of the joints that results from using these adhesives. The article is divided into sections based on the following classifications: market economics, adhesion, pressure-sensitive adhesives, hot-melt adhesives, solution-based adhesives, structural adhesives, and natural product-based adhesives. This final class of adhesives is broader than the first four because it deals mainly with the source of the adhesive material rather than its strength.

## 2. Market Economics

In 2003, the global adhesives and sealants industry was estimated (1) to be about 10 million metric tons (or 22 billion lb). This amount had an estimated market value of \$32.6 billion. In 2007, the global adhesives and sealants market was estimated (2) to be about 15 million metric tons (or 33 billion lb). This market is projected to grow at an aggregate compounded annual growth rate (CAGR) of 3% (3).

In the United States, the adhesives market in 2007 was estimated to be about 3 million metric tons (6.6 billion lb) and to have an approximate value of \$9.5 billion (4). This market value is expected to grow at a CAGR of 6% through 2010. The leading markets in the United States are paper and related products followed by construction, assembly, woodworking, and transportation (5).

Emerging markets, such as China and India, show significant potential for growth in the coming years (2). In 2007, the CAGR in Asia was estimated to be 6%, with the CAGR in China estimated to be more than 10%. (4) Adhesive growth is anticipated to be driven by an increase in automotive manufacturing for weight reduction and new materials (6), in aerospace as they shift to a greater use of composite bonding (7), and in renewable energy (8).

Mergers and acquisitions have continued to consolidate the adhesives and sealants market during the past few years (9). Formulators of adhesives often note that the consolidations of raw materials suppliers require diligence in keeping track of where key ingredients are being made. Moreover, end-users of structural adhesives will have taken notice of adhesive supplier mergers over the past years, because adhesive suppliers seek to provide a more complete product line.

Environmental and regulatory concerns continue to impact adhesive formulators and users alike. Solvent reduction in adhesive processing and use has

adhesives is often *t*-butyl phenolic resin, which—when combined with fillers like MgO—provides a heat resistant formulation (25). Other tackifiers also can be used, but the formulations typically lose in terms of its heat resistance. For the quick grab characteristic of chloroprene-based adhesives, solvent choice becomes important. Not only does the choice of solvent come into the manufacturing of the adhesive, but its evaporation rate also controls the quick grab. Too little solvent in the drying adhesive causes it to lose contact bonding, but too much solvent in the drying adhesive causes it to have too little strength. In addition, too much solvent slows the rate of crystallization. Because of the chlorine in the base resin for these adhesives, acid acceptors such as ZnO and MgO have to be added to the formulation to act as acid neutralizers. At high temperatures, the resin will emit HCl acid, which can cause corrosion of metallic adherends. Adding both these fillers substantially reduces this problem.

Neoprene Contact-Bond adhesives are used in many applications from laminating, to shoe manufacture, and to home construction.

## 7. Structural Adhesives

A structural adhesive is an adhesive that forms a permanent bond between two substrates with overlap shear strength greater than 1000 psi (26). Structural adhesives are desirable in load bearing applications, because they provide a suitable substitute for welding or mechanical fasteners by eliminating stress concentrations, which allows for the joining of dissimilar materials and a joint that offers superior weatherability. The key classes of structural adhesives include epoxies, acrylates, urethanes, and phenolics. Hybrid adhesives incorporate two or more of these classes of structural adhesives.

**7.1. Epoxy Resins.** The first synthetic epoxy resin was described in a U.S. Patent in 1943 by Pierre Castan, later attributed to Ciba (27). The most common form of epoxy resin is based on the diglycidyl ether of bisphenol A (DGEBA). This resin is produced from a reaction of bisphenol A with epichlorohydrin, in which the epichlorohydrin endcaps the bisphenol A and provides the glycidyl ether reactive group of the epoxy. By adjusting the ratios of bisphenol A to epichlorohydrin, the molecular weight of the epoxy, and subsequently the epoxy equivalent weight (EEW), can be adjusted. The most common liquid epoxy resin is the product of one stoichiometric equivalent of bisphenol A with two stoichiometric equivalents of epichlorohydrin with an EEW of 170. A mono-disperse product will lead to crystallization, so resin manufacturers often add slight amounts of higher molecular weight fractions to prevent crystallization, which leads to an EEW between 180 and 195. Most liquid DGEBA resins will have a molecular weight of less than 450. Higher molecular weight resins are solid. To adjust the viscosity of epoxy resins, formulators add diluents, which can either be nonreactive or reactive (commonly with either mono or difunctional reactivity).

Although DGEBA resins are more common, a significant amount of epoxies are available beyond this chemistry. Epoxies can be either mono, di, or polyfunctional in reactive end groups. The backbone of the epoxy resin can be aliphatic, cyclic, or aromatic in nature. Brominated (28) or phosphated (29) epoxies can be

used to obtain flame resistance. Specialty epoxy adhesives can be based on epoxy resins reacted with dimer acids, urethanes, or other reactive elastomers to achieve greater flexibility. Most adhesives are stable up to 200°C.

Epoxies can be formulated into either a one- or two-part format. These formulations commonly are referred to as 1K and 2K, respectively. The one-part format contains a latent curative and can be in either a paste or solid form. Two-part epoxy adhesives are often in a liquid or paste form with the curative on the A-side and the epoxy resin on the B-side. When the two parts are mixed, the epoxy resin is reacted to form the adhesive.

The most common reactive functionality of the adhesive is a glycidyl ether or glycidyl ester because they react with most curatives. The strained oxirane ring is reactive with functional groups with either nucleophilic (basic) or electrophilic (acidic) character. Other epoxy reactive groups can be used (such as cycloaliphatic) but require specialized curatives.

Curing agents are called hardeners and are responsible for cross-linking the epoxy network. They either can promote direct cross-linking or catalyze homopolymerization (chain extension) of the epoxy network. Acid anhydrides, carboxylic groups, tertiary amines, and hydroxyl groups react slowly with the oxirane ring, and typically are used as catalysts for this reason. Amines and mercaptans react rapidly with the oxirane ring, and their reaction can be enhanced through the use of the catalysts mentioned. The epoxy resin and curative package as well as the cure time and temperature influence the cure speed and final glass transition temperature ( $T_g$ ) of the adhesive.

One-part epoxy adhesives usually consist of DGEBA, a diluent, and a latent curing agent that is either insoluble with the resin at room temperature or is sterically hindered or chemically blocked at room temperature. When the curing agent reaches a higher temperature, it melts into the adhesive or the reactive group becomes free, which triggers the cure of the epoxy. One-part epoxies are common in aerospace, automotive, and electronics manufacturing where heat curing is available readily through the manufacturing process.

Dicyandiamide is the most frequent latent curative used in epoxies. It commonly is referred to as "dicy," and readily reacts at 180°C. The size of dicyandiamide particles can impact the cure temperature, rate of cure, and shelf stability. Other latent curatives include metal complexed imidazoles, crystallized amine (30), complexes of Lewis acids (such as  $\text{BF}_3$  with amine), and diaminodiphenylsulfone. Dihydrazides, such as isophthalic dihydrazide, cure at 100–110°C. Anhydrides also can be used as a curative for epoxies but are hygroscopic in nature (31). The cure can be accelerated, or the curing temperature can be reduced by adding catalysts, such as aromatic tertiary amines, imidazole derivatives, epoxy resin adducts with tertiary and other amines. Examples include Monuron and 3-phenol-1,1,-dimethylurea. Although accelerated 1K epoxies provide a faster or lower temperature cure, they pose potential problems for both the formulator and end-user alike. The formulator must have precise control over the manufacturing process to ensure that viscous mixing does not lead to heating the resin to a point where the latent curative is activated. The adhesive supplier must ship the product to the end-user cold—often on dry ice. Finally, the end-user must store the product cold. In most cases, a lower cure temperature leads to a shorter shelf life of the product.

can be enhanced by adding difunctional or bifunctional cross-linkers or heat-resistant adhesion promoters such as silanes or amines (78). Thickeners also can be added to the cyanoacrylate to improve handling characteristics.

Users of cyanoacrylates often notice how readily it adheres to human skin, which has led to the development of cyanoacrylates as a surgical tool for sutures (79). Suture cyanoacrylates are formulated from butyl cyanoacrylate for its biodegradability (80) and a flexibilizer for tissue bonding. To avoid adhesion of cyanoacrylates to skin (81) in general use, formulators add inhibitors such as alkanols, carboxylic acid esters, or copolymers of maleic acid, vinyl chloride and vinyl acetate.

**7.3. Urethanes.** The key component of a urethane is an isocyanate (82). The isocyanate reacts with alcohols to form urethanes  $[R-NH-CO-O-R']$ , amines to form ureas  $[R-NH-CO-NH-R']$ , thiols to form thiocarbamates  $[R-NH-CO-S-R']$  with amides to form acylureas  $[R-NH-CO-N(R')-CO-R'']$ , urethanes to form allophanates  $[R-NH-CO-N(R')-CO-O-R'']$ , and ureas to form biurets  $[R-NH-CO-N(R')-CO-NH-R'']$ . When isocyanates react with water, they generate unstable carbamic acid that degrades to carbon dioxide, which serves as a basis for polyurethane foams (83). The foundation of urethane chemistry is based on isocyanates.

Polyurethane adhesives can come in as either a one- or two-part formulation. Two-part polyurethanes are based on isocyanates and polyisocyanates that react with diols or polyols to form urethanes. Although toluene diisocyanate (TDI) was used extensively in the past, formulators now are using less toxic isocyanates, such as methylene diphenyl diisocyanate (MDI). Other isocyanates commonly used include hexamethylene diisocyanate (HMDI or HDI), isophorone diisocyanate (IPDI), multifunctional isocyanates, polyisocyanates, isocyanate capped oligomers, and urethane prepolymers. Formulators are keen to minimize the monomeric isocyanate content to reduce potential toxicity issues. Alcohols used in two-part adhesives have an ideal molecular weight between 500 and 3000 and have a backbone of either polyester, polyether, polycarbonate, or polydiene. The cross-linking density of polyurethanes can be increased through the addition of triols (84). Hard/soft segments are introduced to the polyurethane matrix by modifying the backbone of the alcohol, which induces phase separation in the microstructure of the adhesive and leads to improved impact and fatigue resistance (85, 86). The hard/soft segments also can be adjusted to affect the modulus of the polyurethane (87).

The catalyst in a two-part polyurethane controls the rate of the reaction. Tertiary amines promote the isocyanate–water reaction (88), which leads to blowing and foaming of the adhesive. To promote the isocyanate–hydroxyl reaction, formulators commonly add dibutyltin dilaurate (89), stannous octoate (89, 90), and—for curing temperatures higher than 100°C—allophanates and biurets (91). However, these compounds begin to decompose at about 130°C. Uretidiones are catalyzed by bases (91) such as trialkylphosphines, pyridines, and tertiary amines. The reaction of isocyanate trimers is favored through phosphines (92), amines (93), and metal salts such as potassium acetate (94). Polyamines can be added to the polyol to increase cure speed.

One-component urethanes commonly are used as mastics and sealants, and they have a limited use for adhesives. These urethanes are moisture cured from

the atmosphere (83), which promotes the following reaction: Isocyanate reacts with water to form carbamic acid. The carbamic acid decomposes to an amine, which releases carbon dioxide. The amine then reacts with the isocyanate to form a urea, which reacts with the isocyanate to form a biuret and leads to cross-linking. The carbon dioxide produced in the system needs to diffuse out; otherwise, it will lead to foaming. By minimizing the isocyanate content, the cure speed can be balanced with foaming. Cure speeds and foaming rates decrease from the outside in (because the water has to diffuse in to cure), which varies with moisture conditions and relative humidity. Oxazolidine can be added as moisture-activated water scavengers that form hydroxyl and amine groups (95). Blocked isocyanates can be used as polyol curing agents (96) and include phenols, malonates, methylethylketoximine, and caprolactam. The blocking reaction reverses at high temperatures or in the presence of strong nucleophiles, which releases isocyanate. The reactions do not rely on water, do not produce carbon dioxide, but do require heat. Solid polyols also can be used as a latent curative for one-component urethanes, which reacts in at a higher temperature by melting in.

Urethane adhesives give lower oxidative and moisture resistance than epoxies or acrylates. Two-component urethanes are used in automotive, marine, and panel bonding applications. One-component urethanes typically do not have high-temperature stability. Both urethanes are sensitive to hydrolysis. Urethanes contain fillers and pigments to improve handling strength. The transportation industry is the largest user of urethanes, for SMC, FRB, RRIM composites as well as for plastics and windshields. Urethanes also are used for wood bonding. Although the performance of urethanes is on the lower end for structural adhesives, they exhibit high flexibility, strong peel strength, as well as good impact and fatigue resistance. Hybrids of urethanes with other adhesives exhibit these positive attributes as well.

**7.4. Phenolics.** In 1909, the first synthetic structural adhesive—later called Bakelite<sup>TM</sup>—was made by reacting phenol with formaldehyde (97), which formed a phenolic adhesive (98). Resoles and novolacs are the two types of phenolic resins. Resoles (99) commonly are referred to as one-step resins. They are methyl terminated and reacted under basic conditions in an excess of formaldehyde. Self-condensation occurs between 100 and 200°C with a water reduction. Novolacs (100) commonly are referred to as a two-step resin. They are phenol terminated and reacted in acidic reaction conditions with a formaldehyde/phenol molar ratio between 0.5 and 0.8. A curing agent is added in the second part of the process such as hexamethylenetetramine. Formulators can choose from numerous starting materials.

Phenolics are brittle resins. The first successful tougheners for phenolics were based on poly(vinyl formal) powder sprinkled on top of the resol-phenolic bond. These Redux<sup>TM</sup> adhesives (101) were the first toughened thermoset adhesive for aerospace bonding in the 1940s and 1950s—originally pioneered by the Aero Corporation in World War II. In the 1960s, film adhesives were developed from liquid phenolics. Additional tougheners were discovered (98), which included poly(vinyl butyral), nitrile rubbers, polyamides, acrylics, neoprenes, and urethanes.



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